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ESSENTIAL GUIDES TO METHOD DEVELOPMENT IN FLOTATION

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General

This article is designed to develop methods for an interested non-specialist, by showing how they can be used as a basis for a Chemical Engineering Unit Operations course.

Flotation is practised extensively in industry. The technique requires a detailed knowledge in physical metallurgy, the physical chemistry of surfaces, a competence both in mathematics and practical hydrodynamics.

The operation is based simply on the attachment of an air bubble to either a small or low-density particle, or to a liquid droplet.

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Method 1: Selective Separation

Mineral flotation has by far the greatest usage, processing 20 billion tons per year; however the process of delinking newsprint is currently at about 25 million tons per year and is expected to grow significantly in the next decade. In these operations the selective attachment of a bubble to the valuable or an unwanted component of a particle is required. In de-inking, this refers to the removal of ink particles from cellulosic fibres. For mineral processing, a higher degree of selectivity is required, to recover a valuable particle from a suspension of waste particles. This operation is very seldom used on its own but is part of a flowsheet in which, after pretreatment which includes size reduction, a solid suspension in water is fed to the flotation circuit.

In the circuit, cells may be arranged in sequence with each successive cell treating the concentrate from the previous one to improve its purity; this is, called 'roughing'. The final concentrate from the rougher bank is fed to a bank of 'cleaning' cells. The reject stream from the last of the cleaning cells is itself recycled to improve the final recovery and is called 'scavenging'. The concentrate from the final scavenger stream is recirculated to the feed of the first of the rougher cells. The waste from the final scavenging cell is discharged as the overall plant waste. This may be recycled, or treated to minimize its environmental impact. The final cleaner concentrate is essentially the plant product, although it may also have to be processed possibly by recleaning and drying.

In waste paper, de-inking the ink-rich stream tailings appears in what in mineral processing is the concentrate and the de-inked paper in what is usually the mineral processing tailings.

Method 2: Non-Selective Separations

The other class of operations require only the non-selective attachment of air bubbles to a particle/droplet, producing an aggregate of high buoyancy, so that the attached material can be withdrawn from the top of the flotation vessel. Processes of this type include the off-shore recovery of crude oil which may be 5–50% oil by volume, containing dispersed oil in the form of 10–50 μm oil droplets in water. After processing, virtually all the oil is recovered containing only 0–5% water. Other processing operations of this class include water treatment, in which the rate of setting of the flocculants on their own is very slow while the buoyancy of the air bubble/flocculant is high. Also the separation of rejected plastics from general wastes is economically attractive, with polyethylene terephthalate (PET), polyethylene (PE),

polyvinyl chloride (PVC) and polypropylene (PP) being recoverable.

The effectiveness of any flotation separation is described by the fractional recovery of the desired material, R, in the concentrate stream and its purity, the Grade G. The practical application of this is a principle more honoured in the breach than the observance, and is an area where significant economic improvements are possible.

Method 3: Measures of Separation Efficiency Potentially Achievable

In mineral processing, it is convenient to represent both quantities on a plot $0 \leq R, G \leq 1$. The Grade G is defined as $1 - (1 - x_C)/(1 - x_F)$ where x_F and x_C are the mass fractions of the desired component in the feed and concentrate streams respectively, and the fractional recovery of the desired component $R = (Cx_C)/(Fx_F)$. A perfect separation is therefore one in which $R = G = 1$.

Actual simulations lie on the upper boundary of the Grade–Recovery plot and describe the best R at a defined Grade. The area on the plot whose upper boundary represents optimum operation is called the attainable region. The function of the research worker ultimately is to devise techniques whereby the attainable region may be expanded. The Grade–Recovery plot should also be used by operators to monitor and control plant performance. The applications of automatic feed back control is attractive, but the requirements of online instrumentation, such as image processing and chemical analysis detectors, are still in the development stage. This is particularly so with the control actions which are necessary to be able to compensate for deviations from optimum operations. These include changing in air flow rates and the addition of chemicals. It is in this latter area that there is a large measure of uncertainty, which should be addressed as it again offers the possibility of significant economic improvements. The treated tailings which are usually in great bulk still have to be disposed of, at a significant cost, sometimes requiring slime dams to be built or as landfill. This is an environmental factor which may be very costly, both in the operation of existing plants, and in assessing the viability of new projects. Recycling the waste is environmentally acceptable and may also be profitable.

Method 4: Macro Dry Separations

It is significant that siliceous materials can be floated as they may well be the source of gangue contamination in metallic ore flotation. These gangues are in general disadvantageous to the separation and may have to be depressed. However the recycling of simple oxide materials such as corundum, haematite and goethite may well be valuable although floated at lower rates.

Ore-dressing – although this is not strictly a flotation operation – effectiveness determines the limiting separation achievable in the flotation circuit. In the first ore-dressing step, separation is based on size reduction and primary mechanical classification. Once again, the details of the circuit depend on the nature and throughput of the raw material to be processed. The general principles involve crushing followed by dry separation in spirals (which are in fact of a helical design). Crushing and dry separations such as screening are relatively cheap and their use should be maximized to achieve the cheapest possible separation of high value materials from those which are exclusively gangue. Of these dry separation methods, the spirals depend on the difference in density between the waste rock and the valuable material. Vibratory screens may follow or be operated in parallel with the spirals. These are only useful if the fines are largely gangue. The valuable-rich stream from the dry separations is then fed to rod and wet or dry ball mills, the product of which goes to hydrocyclones whose underflow is a solid suspension in water whose solids lie in the size range 50–500 μm. This is a size range at which the subsequent flotation operations will function satisfactorily. The fine product from the mills is aimed at producing two separate powder streams in which there is a sharp change in the valuable material content; this process is referred as the liberation of the valuable material. The power costs of milling are extremely high. The overflow from the cyclones are called slimes and go to settling tanks from which the final solids and liquid wastes may be recycled or discharged. These streams are the primary source of environmental pollution and are vulnerable to objections which may require new treatment techniques.

Method 5: The Characterization of the Solid Material

In flotation, the complete characterization of the solid material to be floated, which varies considerably for different materials, is fundamental to the separation. In paper de-inking the type of ink used and its method of attachment to the waste fibre, determines the nature of the process required. This again is an area in which the technology is still developing. In mineral separations for example, the chemical type of both the valuable material and the gangue have to be identified, and it is also crucial to be able to identify and determine the distribution of individual minerals,

throughout the solid matrix of the primary ore. A mineral may be present as individual grains whose boundaries are a source of mechanical weakness in the solid. This facilitates breakage at the grains following impact and also most interestingly, breakage at the grains following differential thermal effects generated in a microwave field. Alternatively, the mineral may be distributed uniformly throughout the solid matrix. The initial characterization is usually done by microscope examination which, in the hands of an experienced operator, is extremely informative, but which usually has to be supplemented by X-ray fluorescence (XRF) analysis.

Method 6: Wet Processing – Hydrodynamics of Cell Design

The practice of mineral beneficiation by flotation is based on the production of an aqueous suspension of particles in the micron-size range and a dispersion of bubbles in a millimetre-size range. It is the objective within this suspension to achieve particle–bubble collision which will be followed by a selective attachment of the particles. In terms of the method of interception/attachment there are two basic types of cell.

Mechanical Cells

In mechanical cells there is a relatively small inner turbulent region enclosed by a larger diameter quiescent zone. The turbulent region is generated by an impeller which in addition has to disperse air into the solid suspension, and then pump the aerated suspension into the quiescent zone. There are a plethora of designs available which have to be carefully evaluated. The design variations should be related to the achievement of a desired interception/attachment efficiency as a function of particle size. These cells are the most commonly encountered in industrial practice principally because they can have very high capacities, with single cells of up to 300 m^3.

In the inner region the suspension is exposed to a high level of turbulence, in which particle–bubble interception depends on the different paths between the water eddies and the particle trajectories. Although there are no theoretical calculations to provide a basis for these effects, it is assumed that the interception efficiency is determined by the local turbulent intensity and is increased for large particle sizes with a large differential density between the particle and water. Unfortunately, there is a probability that large particles which have been attached to the bubbles, following the turbulent interception may subsequently become detached from the bubble surface. The detachment will be associated with the overall strength of the attachment forces; as these forces are surface effects and the specific surface is low, their detachment probability is high. For the small particles with a high specific surface with an overall high attachment force, the detachment probability is low. It is however, also apparent that these smaller lighter particles, as they follow the eddies closely, will have lower interception efficiencies. The net degree of attachment of particles to bubbles will depend on the design of the agitators (impellers).

Cylindrical Vertical Column Cells

The second cell type takes the form of a cylindrical vertical column in which the suspension is dilute, typically containing 5% solids. In these cells the attachment of a desired particle is more specific than in the mechanical cells. These cells may be between 3 m in diameter and 15 m high. The cells are described by the collection and froth zones. There is also an intermediate zone between the top of the collection zone and the froth. This zone functions very similarly to the top of the collection zone. The solid suspension from the milling circuit is added to the top of the collection zone and the air as bubbles through a sparger at the bottom. The bubbles and particles move countercurrently through the relatively quiescent collection zone. The hydrodynamics of the collection zone are relatively easy to describe. Originally the probability P_c of interception was given by $P_c = 3/2\,(r_p/r_b)^2$ where r_p and r_b are the spherical radii of the particle and bubble, respectively. The original equations have been approximately corrected to allow for gravitational effects in terms of a parameter $K = 2\,(\rho_p r_p^2 U)/(9\mu_f r_b)$ where U is the bubble rise velocity in water of viscosity μ_f and ρ_p is the particle density. P_c indicates some interesting dependencies on K, e.g. (i) there is a K_c which is approximately 1, below which no collision will occur; the smallest size galena particle that can collide with a 1.5-mm bubble is 30 μm; (ii) from the definition of K, when it is $> K_c$, an increase in bubble size will increase the collision efficiency and; (iii) very fine particles follow the streamlines exactly and will only collide if the streamline brings them within 1 particle radius of the bubble. Maximum velocities of 0.9, 1.5, 2.2 and 2.7 mm bubbles have been observed to be respectively 25.0, 36.5, 3.47 and 32.0 cm s^{-1}. However caution has to be used using predictions based on K as anomalies have been observed, and more accurate equations are now available. Surface-active chemical frothers, e.g. Dowfroth 250 and methyl isobutyl ketone (MIBK), are normally added at concentrations of the order of 30 ppm, these are to stabilize the final froth. The effect of the presence of these frothers

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is to reduce the bubble rise velocity by about 50%. The effect of the surfactants is to adsorb on the bubble surface, increasing the surface viscosity of the water near the bubble, and the bubble rigidity.

Method 7: The Recovery of a Specific Particle Size

The effect of particle size is dependent on interactions with various factors. The ultimate objective is to remove particles of size d_{lib} which is the size at which maximum liberation occurs. Even if the dry separation gives material with a perfect size distribution as the mill feed, there will be a distribution of sizes in the product from the mills, which is the feed to the flotation circuit. If this particle size distribution is $f(d_p)$, the fractional mass of the size d_p, as characterized by their valuable content, then the flotation circuit should aim to maximize the recovery of particles of this size and sizes close to it. Clearly $f(d_{lib})$ should have a maximum and a small standard deviation. Ideally this could take the form of a delta function giving $f(d_{lib}) = \delta(d_{lib}) = 1.0$. The following step is to ensure what spread in the size distribution in the removal of these valuable particles occurs in the flotation circuit. This will depend on the specificity of the interception/attachment efficiency achievable for these particles, with an $f(d)$ size distribution, in a flotation circuit.

The calculation for a specific circuit will depend on the performance of its cells. Consider the specificity of removal of particles in a single mechanical cell. In addition to the interception/attachment in the turbulent zone which has a spread of efficiences, there is also attachment of particles in the quiescent (pulp) zone which may have a different distribution. There is also a restriction on the new upflow rate through the pulp; if it is too high, non-attached particles may be entrained, and if too low the bubble–particle aggregates may settle. The design problem for the cells is firstly to design an impeller which will produce to the optimum size range of valuable particles, while pumping water at a sufficient rate into the pulp for the necessary upflow in the quiescent zone, which as an optimum bubble size distribution, to maximize the recovery of $f(d_{lib})$.

The bubble–particle contact in mechanical cells is sensitive to variations in the size of both, and the cell has to be designed for optimal removal of particle sizes with a high degree of liberation. It is clear that the requirement of the maximum removal of valuable material is not easily met. The mill product will have a distribution of particle sizes, each size with a varying valuable content. The flotation circuit separation should also separate the most valuable particles of a size close to d_{lib}. The design challenge is to design milling and flotation circuits capable of producing and removing a specific size. It is also the responsibility of the operators to ensure that the system is operated continuously at its optimum level. These are realistic objectives.

The separations achievable in columns is potentially far more selective than that of the mechanical cells but are restricted by a narrow operating range. The most effective particle size in a column is of the order of 75 μm with bubble sizes varying from about 0.8 to 2.5 mm. This size range may not be consistent with the peak liberation size. The height of the columns is determined by the need for bubbles to accelerate from the bottom to their terminal velocity, where interception is a maximum. At these conditions the loaded bubbles will entrain into the froth significant amounts of solution containing gangue. The most effective feature of the columns is the removal of these waste solids by adding wash water to the top of the deep froth column. The froth at its top surface will overflow with a maximum grade. In industrial practice, columns are used to upgrade (clean) the froth concentrate from the primary cells (roughers).

Method 8: Pulp Microprocesses

Attachment following the interception of a particle by a bubble depends on the magnitude of the surface forces between them. The characterization of these forces to generate selective attachment is possibly the key factor in the separation.

The particles are always dispersed in water and the nature of the wetting of their surfaces determines the effectiveness of air bubble attachment. For hydrophobic surfaces, the water film is weakly bound and would fail easily after impact, thus causing attachment. The selectivity of the separation can be enhanced by the adsorption of a surface-active agent, a conditioner. These have a polar end which attaches to the solid surface, and a non-polar end which sticks into the water making the surface hydrophobic. In a bubble–particle interception, the particle has a time of contact, the sliding time after the initial interception during which the particle and the bubble will be separated by a thin water film. The sliding time will depend on the initial displacement of the particle from the line of centres of the rising bubble and the settling particle. The rate of thinning will depend on the kinetic energy dissipation after impact and London–van der Waals dispersive forces, electrostatic interactions and capillary forces following distortion of the bubble surface during impact. If the film thins

to a critical thickness, it will fail, which results in a successful attachment. Both the thinning process and the critical thickness depend on the interaction energy at the particle–water interface.

The requirement of hydrophobicity as a basis for attachment is justified by the following theoretical treatment. The dispersion energy $\varepsilon(h_x) = -(1/12\pi)A/h_x^2$. The attraction stress between the two surfaces is then $(\partial\varepsilon(h_x)/\partial h_x) = A/(6\pi h_x^3)$ dynes cm^{-2}. A is the Hamaker constant which is of the order of 10^{-12} ergs. For a condensed system to describe the interaction stress, A is replaced by A_{132} which is a linear combination of two surface interactions only. A_{12} represent the interfacial energy between a particle 1 and a bubble 2 separated by a vacuum, A_{13} and A_{23} are the Hamaker constants representing the particle–water and bubble–water interaction energies respectively. A_{33} is the interaction energy between water molecules. The linear combination $A_{132} = A_{12} - (A_{13} + A_{23} - A_{33})$. If A_{13} and A_{23} representing the particle–water and the bubble–water interactions are low, then A_{132} will be greater than A_{12}. The enhanced attraction between particle and air bubble in the presence of water represents hydrophobic bonding.

Experimental characterization of hydrophobicity can be done using the contact angle. If a liquid droplet is placed on a solid surface at the three-phase point of contact, it will form a definite angle θ between the liquid and solid surfaces, which is called the contact angle. If ΔG^0 is the change in free energy of the three-phase contact, following a small change ΔA_S in the area of contact, then $\Delta G^0 = \Delta A_S(\gamma_{SL} - \gamma_{SV}^0) + \gamma_{LV}\cos(\theta - \Delta\theta)$ at equilibrium; this leads to the Young equation, $\gamma_{SL} - \gamma_{SV}^0 + \gamma_{LV}\cos\theta = 0$. Since γ_{SV}^0 is the energy of contact of a solid with a saturated vapour of partial pressure p^0 there is also present on the surface a film of condensed vapour with its own surface energy π^0. Then the total surface energy of the solid surface is $\gamma_S = \gamma_{SV}^0 + \pi^0$. Substituting in the Young equation for γ_{SL} gives $\gamma_{LV}\cos\theta = \gamma_S - \gamma_{SL} - \pi^0$ in the Dupre equation, the work of adhesion $w_{SLV} = \gamma_{LV}(1 + \cos\theta) + \pi^0$. This relates an increase in θ to a reduction in adhesion energy or alternatively an increase in the surface hydrophobicity.

Electrical Effects

The charge on a solid surface can vary from mineral to mineral and forms a basis for selective separation. The charge is strongly bound close to the surface in the Stern layer while further from the surface the layer is diffuse. If the particle moves in an applied electrical field, a lower potential will be observed which is that at the border of the Stern and the diffuse layers. This is an electrodynamic effect called the ζ potential. The ζ potential is a strong function of pH; the point where the ζ potential is zero is called the PZC (point of zero charge). For goethite (FeOOH) the PZC is 6.7 and at acid pH the zeta potential is positive. Using RSO_3 which has a negative polar group, the recovery of goethite is 100% below pH 4.5 and 0% above pH 6.7, while if dodecylammonium chloride which has a positive polar group is used, the recovery of goethite in acid solution is 0% while above pH 9.5 the recovery is 100%.

The attachment of bubbles to charged electrical surfaces is underresearched. The bubbles are stabilized by surfactants (frothers) whose polar end may be anionic, cationic or non-ionic. The hydrophobic end of their molecule will be inside the bubble while the polar end is in the water. After impact, the previous treatment suggests that if the electrical forces between the bubble and the particle surface are attractive then A_{132} will increase and conversely, if the two surfaces repel each other, A_{132} will decrease. This is mere speculation as experimental confirmation is held up by the extremely small frother concentrations on the bubble surface, and the difficulty in the determination of the bubble's charge.

Method 9: Froth Microprocesses

As the particle–bubble aggregates rise to the top of the pulp they entrain with them in their boundary layers a small but significant amount of the pulp suspension which contains both unattached valuable and waste particles. The bubbles loaded with valuable solids pass through the upper level of the pulp and form a froth. As they pass into the froth, they entrain with them pulp water. In the froth the void volume of the pulp suspension is reduced from that in the pulp, owing to closer packing of the loaded bubbles. This forms the interface between the pulp and the froth which is readily observable (**Figure 1**). The sharp reduction of water in the froth at the point is a preliminary drainage effect. Bubbles will rise through the froth until they either burst at the top surface or, as unbroken bubbles loaded with valuable particles, overflow the concentrate weir. This is the final product of a single cell; the unfloated waste product will settle to the bottom of the quiescent region and leave the cell in the tailings stream.

The performance of the froth depends on the stability of the bubble passing through it. This in turn depends on the amount of frother added. At high levels of frother, the individual bubbles will remain as small spheres and will leave over the concentrate weir essentially unchanged from their condition at the bottom of the froth. Their water content will therefore be unchanged and there will be no upgrading of

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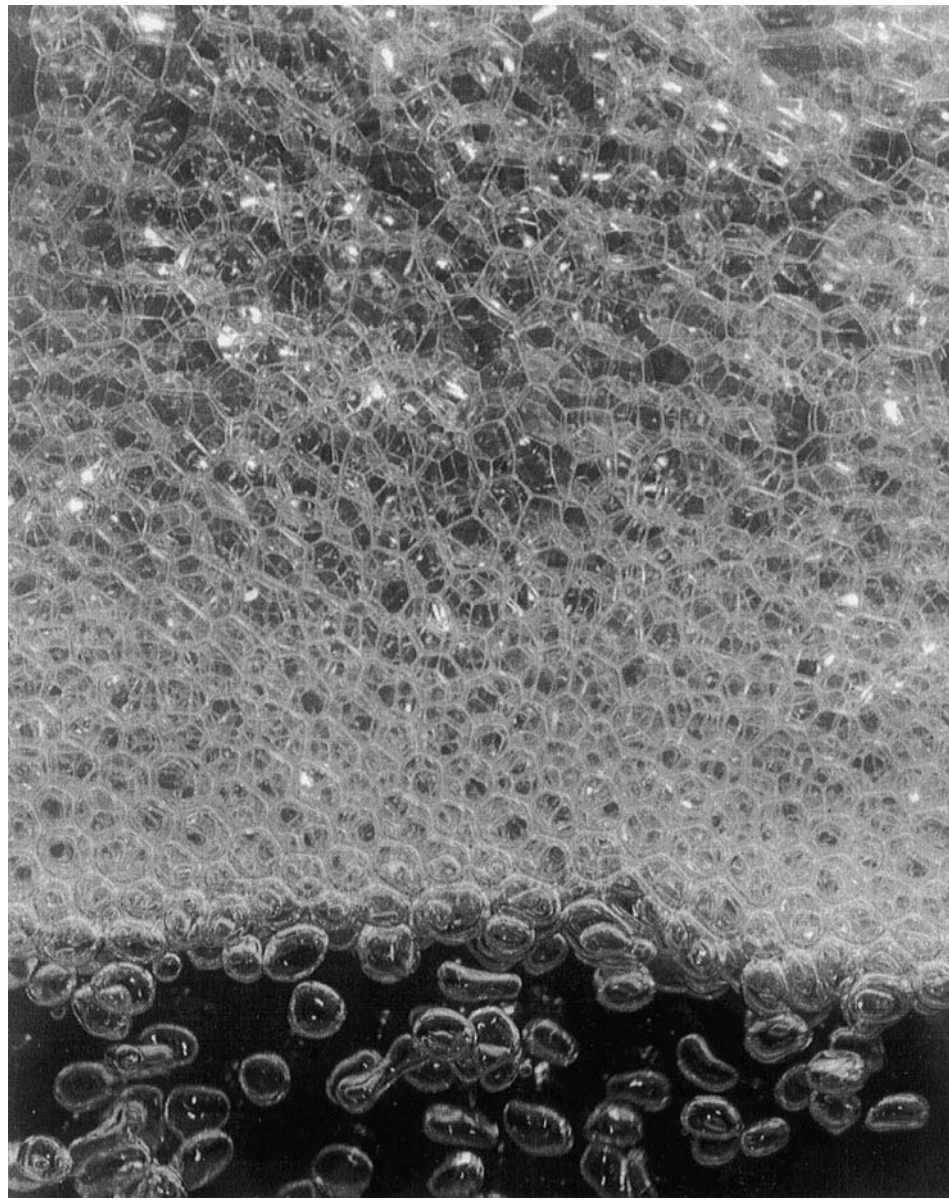

Figure 1 Pulp–froth interface.

the solid product. They will not burst at the top surface of the froth and will flow easily over the weir. With a lower level of frother addition, the spherical bubbles will deform to non-coalescing dodecahedra. The flat faces of the bubbles will be separated by lamellae with a size in microns (**Figure 2**). Water squeezed down the lamellae, flows into plateau borders which are of millimetre size; the three plateau borders at their ends join to form nodes down a network of which the entrained froth water drains back to the pulp. It has been reported that for two-phase foams, that the volumetric water content of the foam will fall from 0.26, at 5 mm from the pulp–foam interface to 0.016, at 12 cm from the bottom of the foam. After that the value of 0.016 will remain constant through the foam. For coalescing foams the bubbles moving towards the weir will continue to grow, giving a lower volumetric water contents of < 0.01. The effect of coalescence in a three-phase froth, will therefore be to increase the Grade, G, but with a decrease in fractional recovery, R, because of bubble breakage at the top surface of the froth.

Finally it may be observed that cells may potentially be controlled automatically with online image processing cameras.

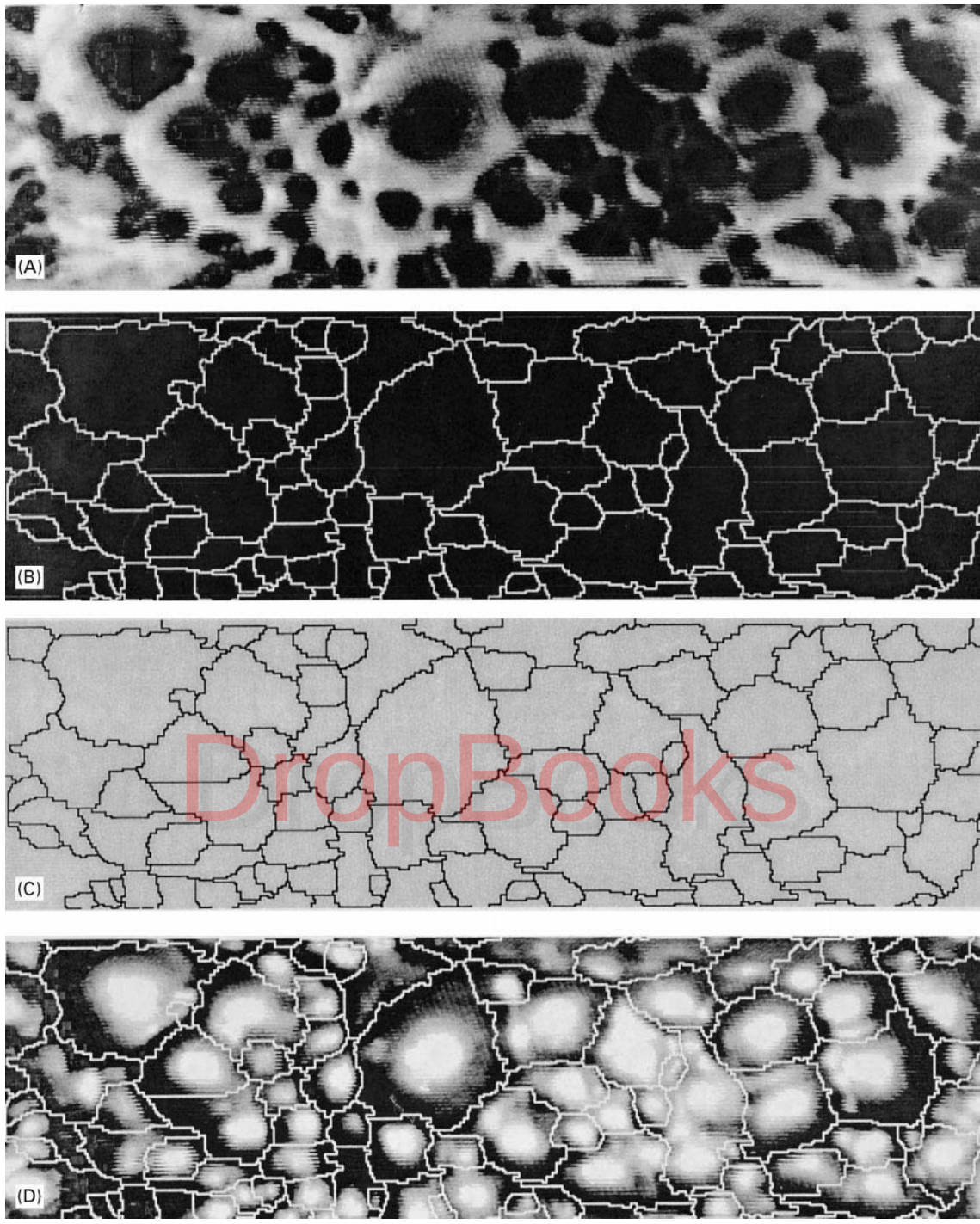

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Figure 2 Control of flotation cells by image processing the upper surface of their froths. (A) The bubble structure in inverted light and the same structure with bubble boundaries sharply demarcated. (B) and (C) A comparison between the image-processed bubble structures, in inverted and reflected light, respectively. (D) The bubble structure in reflected light with image-processed boundaries superimposed.

See also: **I/Flotation. II/Flotation:** Bubble-Particle Adherence: Synergistic effect of Reagents; Bubble-Particle Capture; Column Cells; Cyclones for Oil/Water Separations; Dissolved Air; Foam Fractionation; Froth Processes and the Design of Column Flotation Cells; Historical Development; Hydrophobic Surface State Flotation; Intensive Cells: Design; Oil and Water Separation; Reagent Adsorption on Phosphates. **III/De-inking of Waste Paper: Flotation.**